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(54) Title: COMPOSITION BASED ON WATER-DISSIPATABLE ACRYLIC POLYMER (57) Abstract <p>A composition comprising water-dissipatable acrylic polymer, water, colorant, a water-miscible organic solvent and a water-immiscible organic solvent. The composition may be used in thermal and piezo ink jet printers.</p>		

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COMPOSITION BASED ON WATER-DISSIPATABLE ACRYLIC POLYMER

This invention relates to compositions containing certain acrylic polymers and to their use in ink jet printing.

Ink jet printing methods involve a non-impact printing technique for printing an image onto a substrate using ink droplets ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for colorants and inks used in ink jet printing. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle. The most popular ink jet printers are the thermal and piezoelectric ink jet printers.

There is a need for inks which are suitable for both thermal and piezo ink jet printers, have high colour strength and produce images having a high light-fastness and water-fastness when printed on a substrate. Many inks will not work in thermal ink jet printers, tending to foul the heater element and block the nozzles.

According to a first aspect of the present invention there is provided a composition comprising a water-dissipatable acrylic polymer water, colorant, a water-miscible organic solvent and a water-immiscible organic solvent.

The Acrylic polymer

The water-dissipatable acrylic polymer has preferably been obtained from the polymerisation of one or more olefinically unsaturated monomers having water dispersing groups, optionally in the presence of one or more olefinically unsaturated monomers which are free from water dispersing groups.

Preferably the number average molecular weight (Mn) of the acrylic polymer is less than 25,000, more preferably is less than 20,000, especially less than 15,000. The Mn of the acrylic polymer may be measured by gel permeation chromatography ("gpc").

The gpc method used for determining Mn preferably comprises applying the acrylic polymer to a chromatography column packed with cross-linked polystyrene/divinyl benzene, eluting the column with tetrahydrofuran at a temperature of 40°C and assessing the Mn of the acrylic polymer compared to a number of a polystyrene standards of a known Mn. Suitable cross-linked polystyrene/divinyl benzene chromatography columns are commercially available from Polymer Laboratories.

If the gpc method for determining Mn does not work for any reason, for example the polymer has an unexpected interaction with the gpc column give an unrealistic result, the Mn may be determined using alternative methods, for example by vapour phase osmometry.

5 The acrylic polymer preferably has an acid value of from 0 to 300mgKOH/g, more preferably 20 to 250mgKOH/g, especially 50 to 225mgKOH/g.

The dispersing groups provide the facility of self-dispersibility and solubility to the acrylic polymer in ink media, especially in water. The dispersing groups may be ionic, non-ionic or a mixture of ionic and non-ionic dispersing groups. Preferred ionic
10 dispersing groups include cationic quaternary ammonium groups and acid groups, for example phosphoric acid groups, sulphonic acid groups and carboxylic acid groups.

The dispersing groups may be incorporated into the acrylic polymer in the form of monomers or oligomers bearing the appropriate dispersing groups. One may also react an acrylic polymer which is not water-dissipatable with monomers or oligomers
15 which make the acrylic polymer water-dissipatable.

The acid groups may be subsequently, or during formation of the polymer, fully or partially neutralised with a base containing a cationic charge to give a salt. If the acid dispersing groups are used in combination with a non-ionic dispersing group, neutralisation may not be required. The conversion of any free acid groups into the
20 corresponding salt may be effected during the preparation of the acrylic polymer and/or during the preparation of an ink from the acrylic polymer.

Preferably the base used to neutralise any acid dispersing groups is ammonia, an amine or an inorganic base. Suitable amines are tertiary amines, for example triethylamine or triethanolamine. Suitable inorganic bases include alkaline hydroxides
25 and carbonates, for example lithium hydroxide, sodium hydroxide, or potassium hydroxide. A quaternary ammonium hydroxide, for example $N^+(CH_3)_4OH^-$, can also be used. Generally a base is used which gives the required counter ion desired for the composition which is prepared from the acrylic polymer. For example, suitable counter ions include Li^+ , Na^+ , K^+ , NH_4^+ and substituted ammonium salts (including tetra
30 substituted amines, e.g. $(CH_3)_4N^+$).

Non-ionic dispersing groups may be in-chain, pendant or terminal groups. Preferably non-ionic dispersing groups are pendant polyoxyalkylene groups, more preferably polyoxyethylene groups. The non-ionic groups may be introduced into the acrylic polymer in the form of a compound bearing non-ionic dispersing groups and at
35 least one (although preferably only one) copolymerisable olefinically unsaturated group.

The nature and level of dispersing groups in the acrylic polymer influences whether a solution, dispersion, emulsion or suspension is formed on dissipation of the acrylic polymer.

The dispersing group content of the acrylic polymer may vary within wide limits but is preferably sufficient to enable the acrylic polymer to form stable ink-jet printing inks in water and aqueous media. The acrylic polymer is preferably soluble in water, although minor amount of the acrylic polymer may be insoluble in water and exist as
5 dissipated particles when mixed with aqueous media or water.

Preferably the proportion of insoluble, water-dissipatable acrylic polymer is less than 50%, preferably less than 40% and most preferably less than 30% by weight relative to the total weight of the acrylic polymer. The size of insoluble acrylic polymer
10 particulates when dissipated in an ink is preferably less than 100nm, and more preferably less than 60nm.

When the acrylic polymer is prepared by polymerisation (a) olefinically unsaturated monomers providing dispersing groups in the presence of (b) olefinically unsaturated monomers which are free from dispersing groups it is preferred that the amount of (b) is from 1 to 95%, more preferably from 2 to 90% by weight relative to the
15 weight of (a) + (b).

The acrylic polymer may be prepared in a conventional manner by polymerising the olefinically unsaturated monomers providing dispersing groups either alone or in the presence of olefinically unsaturated monomers which are free from dispersing groups. Temperatures of from 20°C and 180°C are preferred. The polymerisation may be
20 continued until reaction between the monomers is complete.

In one embodiment the acrylic polymer may be prepared by polymerising an acrylic oligomer having water dispersing groups and one olefinically unsaturated terminal group in the presence of one or more olefinically unsaturated monomers which are free from water dispersing groups and/or olefinically unsaturated monomers having
25 water dispersing groups. Alternatively an acrylic oligomer which is free from water dispersing groups may be polymerised in the presence of one or more olefinically unsaturated monomers having water dispersing groups.

Preferred polymerisation methods include solution polymerisation, emulsion polymerisation, suspension polymerisation and solution/dispersion polymerisation and
30 such general methods are well known in the art.

If desired an initiator may be used to assist acrylic polymer formation. Suitable initiators are free-radical generators. Examples of catalysts include azobis compounds, peroxides, hydroperoxides, redox catalysts, etc., for example, potassium persulfate, ammonium persulfate, tert-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate,
35 2,4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide, dicumyl peroxide, azobisisobutyronitrile, azobis(2-amidino-propane)hydrochloride and the like.

Typically 0.05 to 5% by weight of initiator is used relative to the total weight of the monomers. Preferably the polymerisation is performed in the presence of an emulsifying agent.

5 The Mn of the acrylic polymer may be controlled by the addition of chain transfer agents and/or through the adjustment of the ratio of the concentration of monomers relative to the concentration of initiator during the course of the polymerisation. Typical chain transfer agents are thiols, halocarbons and cobalt macrocycles.

Preferred Monomers

10 Preferred olefinically unsaturated monomers providing ionic dispersing groups include acrylic acid, methacrylic acid, itaconic acid, maleic acid, monoalkyl itaconates (for example, monomethyl maleate, monoethyl maleate, monobutyl maleate and monooctyl maleate), citraconic acid, styrenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid, acryloyloxyalkyl sulfonic acids (for example, acryloyloxymethyl
15 sulfonic acid, acryloyloxyethyl sulfonic acid, acryloyloxypropyl sulfonic acid and acryloyloxybutyl sulfonic acid), methacryloyloxymethyl sulfonic acid, methacryloyloxyethyl sulfonic acid, methacryloyloxypropyl sulfonic acid and methacryloyloxybutyl sulfonic acid), 2-acrylamido-2-alkylalkane sulfonic acids (for example, 2-acrylamido-2-methylethanesulfonic acid, 2-acrylamido-2-methylprop-
20 panesulfonic acid and 2-acrylamido-2-methylbutane sulfonic acid), 2-methacrylamido-2-alkylalkane sulfonic acids (for example, 2-methacrylamido-2-methylethanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid and 2-methacrylamido-2-methylbutanesulfonic acid), mono-(acryloyloxyalkyl)phosphates (for example, mono(acryloyloxyethyl)phosphate and mono(3-acryloyloxypropyl)phosphates) and
25 mono(methacryloyloxyalkyl)phosphates (for example, mono(methacryloyloxyethyl)phosphate and mono(3-methacryloyloxypropyl)phosphate).

Preferred olefinically unsaturated monomers providing non-ionic dispersing groups include alkoxy polyethylene glycol (meth)acrylates, preferably having a number
30 average molecular weight of from 350 to 2000. Examples of such monomers which are commercially available include ω -methoxypolyethylene glycol acrylate (mean polymerisation degree of polyethylene glycol is about 9) and diethylene glycol vinyl ether.

Preferred olefinically unsaturated monomers which are free from dispersing groups include alkyl(meth)acrylates, optionally substituted styrenes, methacrylamides,
35 allyl compounds, vinyl ethers, vinyl ketones, vinyl halides, olefins and unsaturated nitriles.

Preferred alkyl(meth)acrylates contain less than twenty carbon atoms. Examples include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl, sec-butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate,

octyl acrylate, tert-octyl acrylate, 2-phenoxyethyl acrylate, 2-chloroethyl acrylate, 2-bromoethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, 2-chlorocyclohexyl acrylate, acrylate, cyclohexyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, hydroxyethyl(methyl)acrylate, hydroxypropyl(meth) acrylate, 5-hydroxypentyl acrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-ethoxyethyl acrylate, 2-iso-propoxyethyl acrylate, 2-butoxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, 2-(2-butoxyethoxy)ethyl acrylate, 1-bromo-2-methoxyethyl acrylate, 1,1-dichloro-2-ethoxyethyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate benzylmethacrylate, chlorobenzyl methacrylate, octyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, 2-(3-phenylpropyloxy)ethyl methacrylate, dimethylaminophenoxyethyl methacrylate and furfuryl methacrylate.

Preferred optionally substituted styrenes include styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, acetoxymethylstyrene, methoxystyrene, 4-methoxy-3-methylstyrene, dimethoxystyrene, chlorostyrene, dichlorostyrene, trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, trifluorostyrene and 2-bromo-4-tri-fluoromethylstyrene.

Preferred methacrylamides contain less than 12 carbon atoms. Examples include methylmethacrylamide, tert-butylmethacrylamide, tert-octylmethacrylamide, benzylmethacrylamide, cyclohexylmethacrylamide, phenylmethacrylamide, dimethylmethacrylamide, dipropylmethacrylamide, hydroxyethyl-N-methylmethacrylamide, N-methylphenylmethacrylamide, N-ethyl-N-phenylmethacrylamide and methacrylhydrazine.

Preferred allyl compounds include allyl acetate, allyl caproate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, allyl lactate, allyloxyethanol, allyl butyl ether and allyl phenyl ether.

Preferred vinyl ethers contain less than 20 carbon atoms. Examples include methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether and dimethylaminoethyl vinyl ether.

Preferred vinyl ketones contain less than 12 carbon atoms. Examples include methyl vinyl ketone, phenyl vinyl ketone and methoxyethyl vinyl ketone.

Preferred vinyl halides include vinyl chloride, vinylidene chloride and chlorotrifluoro ethylene.

Preferred olefins include unsaturated hydrocarbons having less than 20 carbon atoms. Examples include dicyclopentadiene, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 5-methyl-1-nonene, 5,5-dimethyl-1-octene, 4-methyl-1-hexene, 4,4-dimethyl-1-pentene, 5-methyl-1-hexene, 4-methyl-1-heptene, 5-methyl-1-heptene, 4,4-dimethyl-1-hexene, 5,5,6-trimethyl-1-heptene, 1-dodecene and 1-octadecene.

Preferred unsaturated nitriles include acrylonitrile and methacrylonitrile

The preferred olefinically unsaturated monomers which are free from dispersing groups are the alkyl (meth)acrylates containing less than 20 carbon atoms, especially those specifically listed above.

The acrylic polymer of the present invention may be purified if desired in the usual way for colorants used in ink jet printing inks. For example a mixture of the acrylic polymer and water may be purified by ion-exchange, filtration, reverse osmosis, dialysis, ultra-filtration or a combination thereof. In this way one may remove co-solvents used for the polymerisation, low molecular weight salts, impurities and free monomers.

The Colorant

The colorant is preferably soluble in the acrylic polymer. Preferably the colorant is soluble in organic solvents and insoluble in water, for example it is free from sulpho and carboxy groups. In a preferred embodiment the colorant is a dye, more preferably a dye which is soluble in organic solvents and insoluble in water, especially a disperse dye.

The colorant is preferably yellow, magenta, cyan or black.

The colorant may be a single coloured component or a mixture of coloured components, for example it may be a mixture of different dyes. By using a mixture of different dyes as the colorant one may achieve greater flexibility in colour of the ink.

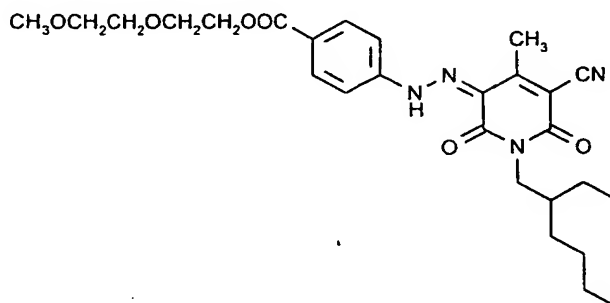
Useful classes of colorants include anthraquinones, phthalocyanines, pyrrolines, triphenyldioxazines, methines, benzodifuranones, coumarins, indoanilines, benzenoids, xanthenes, phenazines, solvent soluble sulphur dyes, quinophthalones, pyridones, aminopyrazoles, pyrrolidines, styrylics and azoics. Examples of preferred azoics are monoazo, disazo and trisazo disperse dyes each, of which are optionally metallised and solvent soluble dyes; especially preferred azoics contain heterocyclic groups. The Colour Index International lists suitable disperse and solvent soluble dyes, examples of which include Solvent Blue 63, Disperse Blue 24, Solvent Black 3, Solvent Black 35 and Disperse Red 60.

Further examples of disperse dyes are given in the Colour Index, 3rd Edition, Volume 2, pages 2483 to 2741 and further examples of solvent soluble dyes are given in

Volume 3, pages 3566 to 3647 and each of these dyes is included herein by reference thereto.

Preferred colorants for use in the inks include:

CuPc(SO₂NHCH₂CH₂CH₂N(CH₃)_{2.7}(SO₃H)_{0.3} in which Pc is phthalocyanine; and



Water-Miscible Organic solvents

Suitable water-miscible organic solvents include C₁₋₅-alkanols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol and isobutanol; amides, e.g. dimethylformamide and dimethylacetamide; ketones and ketone alcohols, e.g. acetone and diacetone alcohol; C₂₋₄-ether, e.g. tetrahydrofuran and dioxane; alkylene glycols or thioglycols containing a C₂-C₆ alkylene group, e.g. ethylene glycol, propylene glycol, butylene glycol, pentylene glycol and hexylene glycol; poly(alkylene glycol)s and thioglycol)s, e.g. diethylene glycol, thiodiglycol, polyethylene glycol and polypropylene glycol; polyols, e.g. glycerol and 1,2,6-hexanetriol; and lower alkyl glycol and polyglycol ethers, e.g. 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy)ethanol, 3-butoxypropan-1-ol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol; cyclic esters and cyclic amides, e.g. optionally substituted pyrrolidones; sulpholane; and mixtures containing two or more of the aforementioned water-miscible organic solvents. Preferred water-miscible organic solvents are C₁₋₆-alkyl mono ethers of C₂₋₆-alkylene glycols and C₁₋₆-alkyl mono ethers of poly(C₂₋₆-alkylene glycols).

Water-immiscible Organic Solvents

Suitable water-immiscible organic solvents include aromatic hydrocarbons, e.g. toluene, xylene, naphthalene, tetrahydronaphthalene and methyl naphthalene; chlorinated aromatic hydrocarbons, e.g. chlorobenzene, fluorobenzene, chloronaphthalene and bromonaphthalene; esters, e.g. butyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate, benzyl benzoate, butyl benzoate, phenylethyl acetate, butyl lactate, benzyl lactate, diethyleneglycol dipropionate, dimethyl phthalate, diethyl

phthalate, dibutyl phthalate, di (2-ethylhexyl) phthalate, alcohols having six or more carbon atoms, e.g. hexanol, octanol, benzyl alcohol, phenyl ethanol, phenoxy ethanol, phenoxy propanol and phenoxy butanol; ethers having at least 5 carbon atoms, preferably C₅₋₁₄ ethers, e.g. anisole and phenetole; nitrocellulose, cellulose ether, cellulose acetate; low odour petroleum distillates; turpentine; white spirits; naphtha; isopropylbiphenyl; terpene; vegetable oil; mineral oil; essential oil; and natural oil; and mixtures of any two or more thereof. Benzyl alcohol is especially preferred.

Preferred Formulations

The composition according to the first aspect of the invention may be prepared by mixing the acrylic polymer, colorant, water, water-miscible organic solvent and water-immiscible organic solvent in any order. Suitable mixing techniques are well known in the art, for example agitation, ultrasonication or stirring of the components. The acrylic polymer may be present in the composition in any form, especially suitable for use in inkjet printing (including a form suitable for dilution to give an ink jet printing ink), for example the form of a dispersion, emulsification, suspension, solution or a combination thereof.

Preferably the composition is prepared by mixing a dissipation of the acrylic polymer in a first liquid medium with a solution of the colorant in a second liquid medium, wherein the first liquid medium comprises water and optionally a water-miscible organic solvent and the second liquid medium comprises a water-immiscible organic solvent and optionally a water-miscible organic solvent.

The weight ratio of water-miscible organic solvent to water-immiscible organic solvent in the ink is preferably 19:1 to 1:1, more preferably 8:1 to 1:1, especially 5:1 to 1:1.

The amount of colorant and water-dissipatable acrylic polymer contained in the composition will vary according to the depth of shade required. Typically, however, the composition will comprise:

- (a) from 0.5 to 50 parts, more preferably 2 to 20 parts, of a water-dissipatable acrylic polymer (preferably having a weight average molecular weight less than 50,000 or Mn less than 25,000);
- (b) from 0.1 to 20 parts, more preferably 0.5 to 10 parts, especially 0.5 to 3 parts of colorant;
- (c) from 40 to 90 parts, more preferably from 50 to 80 parts of water;
- (d) from 2 to 30 parts, more preferably 5 to 15 parts, especially from 8 to 12 parts of a water-immiscible organic solvent; and
- (e) from 2 to 60 parts, more preferably from 5 to 25 parts, especially from 10 to 20 parts of a water-miscible organic solvent;

wherein all parts are by weight and the total number of parts of (a) + (b) + (c) + (d) + (e) add up to 100.

The number of parts of the water-dissipatable acrylic polymer is calculated on a 100% solids basis. For example 50g of a 20% solids acrylic polymer is taken as 10g of acrylic polymer.

5 The composition optionally contains further ingredients of the type commonly used in ink jet printing inks, for example a biocide, for example Proxel GXL (Proxel is a trade mark of Zeneca Limited) or Kathon (Kathon is a trade mark of Rohm and Haas), a fungicide, a rheological agent, e.g. a wax (e.g. beeswax), a clay (e.g. bentonite), an IR absorber, for example Projet 900NP (Projet is a trade mark of Zeneca Limited), or a fluorescent brightener, for example C.I. Fluorescent Brightener 179 and/or UV absorber, for example hydroxy phenylbenzotriazole. Furthermore the ink compositions optionally contain a surface active agent, wetting agent and/or an emulsifier, for example those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3rd Edition 1996 each of which is incorporated herein by reference.

10 The composition preferably has a pH from 3 to 11, more preferably from 4 to 10. The pH selected will depend to some extent on the desired cation for colorant and the materials used to construct the ink jet printer head. The desired a pH may be obtained by the addition of an acid, base or a pH buffer. Where a base is used this is preferably the same base as was used to neutralise the anionic dispersing group during the preparation of the acrylic polymer.

20 The viscosity of the composition is preferably less than 20cp, more preferably less than 15cp, especially less than 10cp, at 20°C.

The composition of the present invention may be used for piezoelectric, thermal and continuous ink jet printers. Many other compositions based on polymers work poorly or even not at all in thermal ink jet printers.

25 Compositions of the invention form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the inks show good storage stability, wet and light fastness and fastness to both acidic and alkaline highlighter pens.

30 Preferably the composition has been filtered through a filter having a mean pore size less than 10µm, more preferably less than 5µm, especially less than 1µm. In this way particulate matter which could otherwise block the printer-head is removed.

Preferably the composition is an ink (especially an ink jet printing ink) or a liquid concentrate which may be used to prepare such an ink.

35 A further aspect of the invention provides a process for printing an image on a substrate comprising applying thereto a composition according to the first aspect of the present invention by means of an ink jet printer.

The ink jet printer preferably applies the composition to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet

printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the composition in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the composition to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the composition from the nozzle.

The substrate is preferably a paper, plastic, or textile material, more preferably a paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character. Most preferably the substrate is a coated paper.

According to a further feature of the invention there is provided an ink jet printer cartridge containing a composition as hereinbefore defined.

The invention will now be described by example only. All parts and percentages are by weight unless specified otherwise. In the examples, compounds referred to by reference to CI numbers are the dyestuffs identified by these numbers in the Colour Index International, 3rd Edition, 3rd Revision.

Example 1

Preparation of Water-dissipatable acrylic terpolymer: BA/MMA/AA = 50/35/15 (%W/W)

Stage 1

Component Number	Component Name	Amount (g)
1	Butyl acrylate	112.79
2	Methylmethacrylate	78.46
3	Acrylic acid	33.75
4	Butyl acetate	535
5	3-Butylmercaptan	6.75
6	AIBN	2.25

AIBN is azo bisisobutyronitrile.

1,2,3,4 and 6 were added to a one-litre baffled round bottomed flask fitted with a stirrer and condensor and slowly heated under agitation and a flow of dry nitrogen up to the reaction temperature of 80°C. After 3 hours at this temperature the polymerisation was complete. The solids content was 29.8%w/w.

The mixture was allowed to cool, before removing the butyl acetate by rotary evaporation to yield a water-dissipatable acrylic polymer as a viscous resinous material. The polymer was found to have an Mn of 4980; Tg=-13.7C, acid value=115mgKOH/g ("Resin 1").

Resin 1 (30g) was then added to a solution of ammonia (4g) in water (66g) and allowed to dissolve with mild agitation and heating to give a 30%w/w solids dissipation in water.

5 Stage 2 - Preparation of Ink 1

A sample of a solvent soluble phthalocyanine dye (3g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. A mixture of Resin 1 from Stage 1 (30g, 30%w/w dissipation in water) adjusted to pH 9.5 and water (37g) were added and the mixture was shaken to give Ink 1 having the formulation:

10

<u>Component</u>	<u>Amount (g)</u>
Dye	3
Resin 1	30 (30% solids)
Benzyl alcohol (Immiscible)	10
2-pyrrolidone (Miscible)	20
Water	<u>37</u>
	<u>100</u>

15

Examples 2 to 6

20 Stage 1

The method described in Example 1, Stage 1, was repeated except that the following components were used in place of the components described in Example 1, Stage 1:

Component Number	Component Name	Ex 2 Amount (g)	Ex 3 Amount (g)	Ex 4 Amount (g)	Ex 5 Amount (g)	Ex 6 Amount (g)
1	BA	0	0	0	156.25	143.3
2	MMA	180	180	180	22.5	39.4
3	MA	45	45	45	46.25	42.3
4	BAC	535	535	535	535	535
5	3-BM	0	2.25	6.75	6.75	6.75
6	AIBN	2.25	2.25	2.25	2.25	2.25

25

Key BA is n-butylacrylate
 BAC is butylacetate
 MMA is methyl methacrylate
 MA is methacrylate acid

3-BM is 3-butylmercaptan

AIBN is azo bisisobutyronitrile

5 The water dissipatable polymers resulting from Examples 2 to 6 (respectively Resins 2 to 6) had the following properties:

10

Resin	% Solids	Mn	Mw	pH
Resin 2	20	N/M	N/M	9.5
Resin 3	20	8500	16600	9.5
Resin 4	20	5500	10100	9.5
Resin 5	30	6000	9600	8.9
Resin 6	30	6300	10900	8.1

N/M means not measured

15

Stage 2 - Preparation of Inks 2 to 6

Inks were prepared by the method of Example 1, Stage 2, except that there was used the components in the amounts shown in the table below:

Ink	Dye	Resin (g)	Benzyl Alcohol	2-Pyrrolidone	Added Water
Ink 2	3g	Resin 2 (45)	10g	20g	22g
Ink 3	3g	Resin 3 (45)	10g	20g	22g
Ink 4	3g	Resin 4 (45)	10g	20g	22g
Ink 5	3g	Resin 5 (30)	10g	20g	22g
Ink 6	3g	Resin 6 (30)	10g	20g	22g

20

Note: Resins 2, 3 and 4 had a solids content of 20% and Resins 5 and 6 had a solids content of 30%. The dye is the same phthalocyanine dye as that used in Example 1.

25

Comparative Example 1 - High Molecular Weight, Hydrophobic Styrene-Acrylic Preparation of Ink C1

A sample of the phthalocyanine dye used in Example 1 (3g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. A mixture of Neocryl BT44 (20g, obtained from Zeneca Resins, 45%w/w dispersion in water) and water (47g) was added and the mixture was shaken to give Ink C1 having the formulation:

<u>Component</u>	<u>Amount (g)</u>
Dye	3
Neocryl BT44	20 (45% solids)
10 Benzyl alcohol (Immiscible)	10
2-pyrrolidone (Miscible)	20
Water	<u>47</u>
	<u>100</u>

Comparative Example 2 - No acrylic polymer

15 Preparation of Ink C2

A sample of the phthalocyanine dye used in Example 1 (1g) was dissolved in a mixture of benzyl alcohol (10g) and 2-pyrrolidone (20g) using a sonicator. Water (69g) was added and the mixture was shaken to give Ink C2 having the formulation:

<u>Component</u>	<u>Amount (g)</u>
Dye	1
Benzyl alcohol (Immiscible)	10
2-pyrrolidone (Miscible)	20
Water	<u>69</u>
25	<u>100</u>

Ink C2 was found to be unstable to storage overnight with the dye precipitating from soluble. Therefore a freshly prepared sample of ink was used for the tests described in Table 1 below.

30 Example 7 - Ink Jet Printing Using the Inks

Inks 1 to 6 and Inks C1 and C2 were printed onto Conqueror High White Wove plain paper 100g/M² from Arjo Wiggins Limited using a Hewlett Packard thermal ink-jet printer. The properties of the resultant prints are shown in Table 1 below.

35 The prints resulting from Inks 1 and C2 had very good colour strength and brightness (chroma) as indicated in Table 1 and showed very high water fastness. 0.5ml of water run down a test print only 5 minutes after printing produced virtually no stain on the white paper. However Ink C2 suffered from poor storage stability.

Table 1

Ink	Ink stability	Print quality	ROD	Wet rub after 5 min
Ink 1	good	good	0.72	8
Ink 2	good	good	N/M	10
Ink 3	good	good	0.808	10
Ink 4	good	good	N/M	10
Ink 5	good	good	0.85	10
Ink 6	poor	good	0.85	10
Ink C1 (Comparative)	poor	did not fire	X	X
Ink C2 (Comparative)	poor	good	0.907	10

N/M means not measured

5 ROD is the reflected optical density of the resultant print.

Wet rub after 5 minutes was scored 1 to 10 wherein 1 represents poor rub fastness and 10 represents excellent rub fastness.

Example 8

10 Further inks may be prepared having the formulations described in Tables 2 and 3 below wherein the following abbreviations are used. These inks may be applied to plain paper using an ink jet printer.

FRU : fructose

15 Resin* : Identifies which of the acrylic polymers as prepared in Examples 1 to 6 are used.

BZ : Benzyl alcohol

DEG : Diethylene glycol

DMB : Diethyleneglycol monobutyl ether

20 ACE : Acetone

IPA : Isopropyl alcohol

MEOH : Methanol

2P : 2-Pyrrolidone

MIBK : Methylisobutyl ketone

25 SUR : Surfinol 465 (a surfactant)

PHO : K₂PO₄

TEN : triethanolamine

NMP : N-methylpyrrolidone

TDG : Thiodiglycol

CAP : Caprolactam

BUT : Butylcellosolve

5 GLY : Glycerol

Resin : Resin 1 from Example 1 (30% dissipation in water)

Colorant 1 : CuPc (SO₂NHCH₂CH₂CH₂N(CH₂)₃)_{2.7}(SO₃H)_{0.3} wherein Pc is phthalocyanine.

Colorant 2 : The pyridone dye drawn on page 6 above.

TABLE 2

Colorant	Colorant Content	Water	Resin (parts)	BZ	DEG	ACE	NaOH	(NH ₄) ₂ SO ₄	IPA	MEOH	2P	MIBK	BUT
1	2.0	58	1(10)	4	6						10		
2	3.0	61.8	2(10)	5	5		0.2				15		
1	2.1	60.9	1(6)	8							20	1	2
2	1.1	61.9	4(12)	9			0.5				9	5	1
1+2	(3+2)	54	1(5)	15	3	3			6		5	4	
1	5	50	1(15)	20					10				
2	2.4	51.6	1(5)	4		5				6	20	5	1
2	4.1	68.6	1(10)	5	2	10	0.3						
1	3.2	57.8	6(4)	5	4	6			5	4	6	5	
1	5	70	3(10)	6	2	2			1		4		
2	1.8	63.2	1(10)	5							15		5
1	3.3	63.7	5(12)	5		5				2		6	3
2	2.0	62.7	1(5)	10		7	0.3		3		10		
2	5.4	49.6	1(4)	20	2	1					15	3	
1	1.0	63	1(7)	5	4						15	5	

TABLE 3

Colorant	Colorant Content	Water	Resin (parts)	BZ	NMP	SUR	TEN	TDG	FRU	PHO	DMB	CH ₃ NH ₂	CAP
2	1.5	63	1(10)	5		0.15	0.5	20					
1	2.5	60	1(15)	6	15					0.12			4
1	3.1	64	1(10)	8		0.3		15				0.2	
2	0.9	63	1(5)	10	20				0.5	0.2			
2	8.0	40	1(15)	15	15			5					2
2	4.0	67	1(10)	10	4				1		4	0.2	
1	2.2	67	1(10)	10	3				2		6		
2	9.0	54	1(15)	9	7		0.5			0.95	5		
2	5.0	57	1(10)	11				10			6		1
1	5.4	54	1(12)	5	17						7		
1	2.1	65	1(15)	5	5	0.1	0.2	2	0.5	0.1	5		
2	2	56	1(10)	10	5			12			5		
1	8	52	1(20)	5	8						5		2
1	10	63	1(13)	2							12		
1	10	71	1(5)	10			1	1				1	1

CLAIMS

1. A composition comprising water-dissipatable acrylic polymer, water, colorant, a water-miscible organic solvent and a water-immiscible organic solvent.
2. A composition according to claim 1 wherein the acrylic polymer has been obtained from the polymerisation of one or more olefinically unsaturated monomers having water dispersing groups, optionally in the presence of one or more olefinically unsaturated monomers which are free from water dispersing groups.
3. A composition according to any one of the preceding claims wherein the colorant is soluble in the acrylic polymer.
4. A composition according to any one of the preceding claims wherein the water-immiscible organic solvent is benzyl alcohol.
5. A composition according to any one of the preceding claims comprising :
 - (a) from 0.5 to 50 parts of a water-dissipatable acrylic polymer
 - (b) from 0.1 to 20 parts of colorant;
 - (c) from 40 to 90 parts of water;
 - (d) from 2 to 30 parts of a water-immiscible organic solvent; and
 - (e) from 2 to 60 parts of a water-miscible organic solvent;wherein all parts are by weight and the total number of parts of (a) + (b) + (c) + (d) + (e) add up to 100.
6. A composition according to any one of the preceding claims wherein the acrylic polymer has a Mn less than 25,000.
7. A composition according to any one of the preceding claims having a viscosity less than 20cp at 20°C.
8. A composition according to any one of the preceding claims for use in ink jet printer.
9. A composition according to any one of the preceding claims which is suitable for use in a thermal ink jet printer.
10. A composition according to any one of the preceding claims which has been filtered through a filter having a mean pore size less than 10µm.

11. An ink jet printing ink according to any one of the preceding claims.
12. A process for printing an image on a substrate comprising applying thereto a
5 composition according to any one of the preceding claims by means of an ink jet printer.
13. An ink jet printer cartridge containing a composition according to any one of
claims 1 to 10.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/00705

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/10 C09D11/00 C08L33/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 769 537 A (SEIKO EPSON CORP) 23 April 1997 see page 4, line 1.4 see page 6, line 10-39 see page 4, line 29 - page 6, line 9 see page 7, line 17-29 ---	1,8,12, 13
A	EP 0 497 522 A (XEROX CORP) 5 August 1992 see page 3, line 55 - page 4, line 5 see page 4, line 8-39 see page 4, line 40 - page 6, line 30 ---	1,8,12, 13
A	US 3 607 813 A (PURCELL CHESTER L ET AL) 11 May 1971 see column 1, line 29 - column 2, line 56 -----	1,2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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